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(54) Title: FLUOROCARBON SILANE HYDROLYSATE-CONTAINING AQUEOUS EMULSIONS, AND MATERIALS COATED THEREWITH			
(57) Abstract			
<p>Aqueous emulsions containing 1) a fluorocarbon silane hydrolysate generated in the presence of a surfactant and 2) a silicate, which provides a clear and smooth coated surface having excellent water repellency and heat resistance when applied to a substrate are disclosed as well as materials coated therewith.</p>			

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TITLE

FLUOROCARBON SILANE HYDROLYSATE-CONTAINING
AQUEOUS EMULSIONS, AND MATERIALS COATED THEREWITH

FIELD OF THE INVENTION

5 The present invention relates to fluorocarbon silane hydrolysate-containing aqueous emulsions. More specifically, it relates both to fluorocarbon silane hydrolysate-containing aqueous emulsions which, when coated and dried on a substrate, are able to provide a water-repelling surface that is clear, smooth, and has an improved heat resistance; as well as to materials obtained by coating and 10 drying this aqueous emulsion on the surface of a substrate.

BACKGROUND OF THE INVENTION

Various proposals have been made concerning silane-containing aqueous solutions that are capable of conferring water and oil repellency to the surface of substrates. A method has been developed (Japanese Kokai No. 4-338,137 [1992]) 15 that uses a solution obtained by mixing a silicon alkoxide having the formula $\text{Si}(\text{OR})_4$, a substituted silicon alkoxide in which some of the alkoxyl groups have been substituted with fluoroalkyl groups, an alcohol, water, and an acid or a base in order to produce water-repellent glass by forming a water-repellent clear film on the surface of a glass substrate. However, this has the drawback that a high 20 concentration cannot be achieved because silicon alkoxide which has been partially substituted with fluoroalkyl groups does not readily dissolve in an alcohol/water-type solvent. Moreover, because this aqueous solution consists of a silicone alkoxide- and alcohol-containing solution in which an acid or a base has been included, the reaction proceeds over time, during the course of which the 25 viscosity rises; hence, the storage stability is poor. In addition, the fact that alcohol is used makes this method environmentally undesirable.

U.S. Patent 5,550,184 discloses emulsions of hydrolyzable alkoxysilane compounds which are able to confer water and oil repellency to a substrate without requiring a special curing operation. However, although these emulsions

are clear immediately after being coated onto a glass sheet, it was found that when thick coatings of these emulsions dry, liquid drops form, making it difficult to maintain the transparency of the glass sheet. In addition, improvements are also desirable in the heat resistance of the coated surface.

5 The present invention provides a stable aqueous emulsion containing a fluorocarbon silane hydrolysate and a silicate which resolves the above-mentioned problems and confers excellent water repellency while maintaining the clarity and smoothness of the coated surface, as well as giving a coated surface which has excellent heat resistance.

10

SUMMARY OF THE INVENTION

The present invention comprises an aqueous emulsion comprising

a) at least one hydrolysate of a fluorocarbon silane having the formula



wherein R_f is a perfluoroalkyl group having from 3 to 18 carbon atoms, or a

15 mixture thereof; each R' is independently an alkyl group having from 1 to 3 carbon atoms; p is from 2 to 4; and n is from 2 to 10; said hydrolysate generated in the presence of a surfactant, and

b) a silicate having the formula

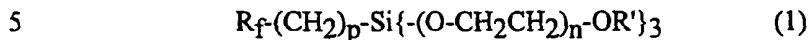


20 wherein each R is independently selected from the group consisting of OCH_3 , OCH_2CH_3 and $(OCH_2CH_2)_mOCH_3$ wherein m is 1 to 10.

The present invention also comprises a water-repellent material which is obtained by coating and drying this aqueous emulsion on a substrate.

DETAILED DESCRIPTION OF THE INVENTION

The fluorocarbon silane hydrolysate-containing aqueous emulsions according to the present invention for resolving the above-described problems contain at least one hydrolysate of a fluorocarbon silane having the formula



wherein R_f is a perfluoroalkyl group having from 3 to 18 carbon atoms, or a mixture thereof; each R' is independently an alkyl group having from 1 to 3 carbon atoms; p is from 2 to 4; and n is from 2 to 10, said hydrolysate generated in the presence of a surfactant, and a silicate having the formula



wherein each R is independently selected from the group consisting of OCH_3 , OCH_2CH_3 and $(OCH_2CH_2)_mOCH_3$ wherein m is 1 to 10.

The fluorocarbon silane hydrolysate-containing aqueous emulsions according to the present invention are those in which the content of the 15 fluorocarbon silane in the aqueous emulsion is from 0.1 to 20% by weight, and the molar fraction of the silicate with respect to the fluorocarbon silane is from 0.3 to 10. Two or more hydrolyzed fluorocarbon silanes may be mixed and used together.

In the aqueous emulsions of the present invention, use is made of, from 20 among hydrolyzable alkoxy silane compounds, those fluorocarbon silanes where R_f is a perfluoroalkyl group having from 3 to 18 carbon atoms. These are preferably perfluoroalkyl groups in which R_f represents mixed perfluoroalkyl groups having an average of from 3 to 12 carbon atoms. R' is a C_1-C_3 alkyl. Preferably R' is methyl, p is 2, and n is from 2 to 4. When n is 2, the preferable 25 fluorocarbon silane hydrolysates are hydrolysates of perfluoroalkylethyltris(2-(2-methoxyethoxy)ethoxy)silanes; when n is 3, the preferable fluorocarbon silane hydrolysates are hydrolysates of 2-perfluoroalkylethyltris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-silanes. This type of fluorocarbon silane is produced by known methods. See Kirk-Othmer, Encyclopedia of Chemical

Technology, third edition, vol. 20, and Mehrota, R. C., Pure Appl. Chem., 13, 111; 1966. The preferred method is by reacting the corresponding perfluoroalkyl trichlorosilane with the proper ether alcohol, such as, diethylene glycol monomethyl ether or triethylene glycol monomethyl ether. The fluorinated trichloro silane starting materials for the above reaction can be prepared by one of several recognized procedures: for example see, McBee, E. T., J. Am. Chem. Soc., 79, 2329 (1957); Adv. Organomet. Chem., 17, 407 (1979); U.S. Patent No. 3,012,006; U.S. Patent No. 4,089,882 or U.S. Patent No. 4,549,003

In order to resolve the problem whereby the above-described fluorocarbon silane forms liquid drops on the glass surface due to homopolymerization, thus causing a loss in the clarity of the glass, and also to enhance the heat resistance in cases where this is applied onto a substrate such as stainless-steel or aluminum, the aqueous emulsions of the present invention contain an ingredient that copolymerizes with the above-described fluorocarbon silane hydrolyzate.

15 Silicates having the formula



in which R represents one or more groups selected from among OCH_3 , OCH_2CH_3 and $(\text{OCH}_2\text{CH}_2)_m\text{OCH}_3$ wherein m is being from 1 to 10, are used in the present invention because they hydrolyze and dissolve in water. The 20 disemulsion of oil-soluble $\text{Si}(\text{OCH}_3)_4$ or $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ in water has hitherto been carried out only in water/alcohol systems, but it was discovered that this generally also hydrolyzes and dissolves in water with at least three hours of stirring. From the standpoint of being able to shorten the stirring time with the hydrolyzed fluorocarbon silane aqueous emulsion and thus enabling easy 25 preparation, water-soluble silicates having the formula $\text{Si}\text{-}\{(\text{OCH}_2\text{CH}_2)_m\text{OCH}_3\}_4$ wherein m is from 1 to 10 are preferable, and water-soluble silicates having the formula $\text{Si}\text{-}\{(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3\}_4$ are especially preferable.

Surfactants are employed to form the stable aqueous emulsions of the 30 fluorocarbon silane hydrolysate which are used in the aqueous emulsions of the

present invention. Emulsions are achieved by emulsifying the hydrolyzable alkoxy silane in water in the presence of an effective amount of surfactant of sufficiently high HLB value to simultaneously retain said hydrolyzable alkoxy silane compound in a substantially totally hydrolyzed state and inhibit said resulting hydrolyzed alkoxy silane compound from self-condensation. Surfactants suitable for use herein are chosen from nonionic, cationic, anionic and amphoteric types. Preferred surfactants are those that have an HLB ("The HLB System" published by ICI America's Inc., Wilmington, Del.; Adamson, A. W., "Physical Chemistry of Surfaces," 4th Ed., John Wiley & Sons, N.Y., 1982, p. 475) value greater than 12, and preferably greater than 16. Surfactants with HLB values from 12 to 16 may be used, but, usually require significantly greater quantities to achieve emulsions of adequate stability. Mixtures of emulsifiers that each meet the above HLB requirements may be used if they are compatible with one another. Suitable emulsifiers include, but are not limited to, alkylbenzenesulfonates, linear alkyldiphenyletherdisulfonates, alpha-olefin sulfonates, ethoxylated alkyl alcohol ethers, ethoxylated alkyl alcohol ether sulfates, ethoxylated alkylphenols, ethoxylated alkylphenol ether sulfates, ethoxylated perfluoroalkylalkanols, C₈-18 alkyltrimethylammonium salts, C₈-18 alkyldimethylammonium salts, ethoxylated C₈-18 amine salts, and alpha-trimethylamino fatty acid betains and perfluoroalkyl amphoteric surfactants of the type R_f-CH₂CH(OR")CH₂N(CH₃)₂CH₂CO₂(inner salt) where R" is H or acetyl, and quaternary salts of the type R_f-CH₂CH₂SCH₂CH(OH)CH₂N(CH₃)₃⁺Cl⁻.

Specific examples that are suitable include nonionic surfactants such as R_f-CH₂CH-O-(CH₂CH₂O)₁₁-H, or C₉H₁₉-C₆H₄-O-(CH₂CH₂O)₅₀-H; cationic surfactants such as R_f-CH₂CH₂SCH₂CH(OH)CH₂N(CH₃)⁺Cl⁻, and anionic surfactants such as C₁₂H₂₅(OCH₂CH₂)₄OSO₃⁻NH₄⁺ and C₁₂H₂₇-C₆H₄-SO₃⁻Na⁺. The R_f in the above surfactants is a perfluoroalkyl group, usually having 3 to 18 carbon atoms. After the aqueous emulsion has been applied to the substrate and dried, it is preferable that the hydrophilic portion within the chemical structure of the surfactant be lost due to heat aging. Because the

hydrophilic polyethylene glycol portions decompose with drying and disappears in a short time, nonionic surfactants having polyethylene glycol hydrophilic portions in the molecular chain are especially preferred.

The fluorocarbon silane content within the aqueous emulsion is at least 5 0.1% by weight, preferably from 2 to 20% by weight, and most preferably from 7 to 15% by weight. When this is less than 0.1% by weight, the water repellency is inadequate, and when this is greater than 20% by weight, it becomes difficult to obtain a stable aqueous emulsion.

The weight ratio within the aqueous emulsion of the fluorocarbon silane 10 and the surfactant employed in the formation of the hydrolysate is from 1:1 to 10:1, preferably from 10:2 to 10:5, and most preferably 10:3. When the ratio of the surfactant is too low, it becomes impossible to keep the aqueous emulsion stable, and when the ratio is too high, hydrophilic groups tend to remain on the substrate even after drying, making it impossible to provide good water 15 repellency.

The molar fraction of the silicate with respect to the fluorocarbon silane is at least 0.1, preferably from 0.3 to 10, and even more preferably from 0.4 to 2. When the ratio of fluorocarbon silane contained is too high, the clarity of the 20 coated surface is lost. If the ratio of the silicate content is too high, the aqueous emulsion gels, resulting in a loss in stability.

The stability of the aqueous emulsion is influenced not only by the 25 fluorocarbon silane concentration and the molar fraction of silicate with respect to the fluorocarbon silane, but also by the pH of the aqueous emulsion and the type of surfactant employed. When a nonionic surfactant is employed any pH is suitable for the stability of the aqueous emulsion. However the pH of the aqueous emulsion can also affect the durability of the coating and then a pH of less than 7 is usually better. Preferably the pH of the aqueous emulsion is less than 4 when a nonionic surfactant is used. When a cationic surfactant is employed, a high pH will negate its surfactant properties and usually the pH of the aqueous emulsion is 30 less than 7, and preferably less than 4. When an anionic surfactant is employed a high pH is usually needed to avoid interaction with the surfactant, and preferably

the pH of the aqueous emulsion is greater than 7, more preferably greater than 10.

In order to obtain a stable aqueous emulsion, the ratios in which the ingredients are included within the aqueous emulsion are set as desired while taking into account all of these conditions.

5 Some desirable examples of stable aqueous emulsions, in cases where a nonionic surfactant represented by the formula $R_F-CH_2-CH_2-O-(CH_2-CH_2-O)_{11}-H$ is used, are aqueous emulsions in which 1) the fluorocarbon silane content is from 0.1 to 20% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 0.1 to 0.5, and the pH has been adjusted to less than 4, 10 and in particular to from 2 to 3, and the weight ratio of fluorocarbon silane and surfactant used to generate the hydrolysate is from 1:1 to 10:1; 2) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 1.0% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 0.1 to 1, the pH has been adjusted to less than 4, and in particular to from 2 to 3, and the 15 weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1; 3) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 2.5% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 0.1 to 1, the pH has been adjusted to from 4 to 7, and the weight ratio of the fluorocarbon silane and the surfactant used to 20 generate the hydrolysate is from 1:1 to 10:1; and 4) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 20% by weight, the molar fraction of the silicate with respect to the fluorocarbon silane is from 0.1 to 5, the pH has been adjusted to 7 or more, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1.

25 In cases where a nonionic surfactant represented by the formula $C_9H_{19}-C_6H_4-O-(CH_2-CH_2-O)_{50}-H$ is used, as long as an aqueous emulsion is used that has a fluorocarbon silane content of from 0.1 to 20% by weight, a silicate molar fraction with respect to fluorocarbon silane of from 0.1 to 5, and a weight ratio of fluorocarbon silane to surfactant used to generate the hydrolysate 30 is from 1:1 to 10:1, this may have any pH.

In cases where a cationic surfactant represented by the formula

$R_f\text{CH}_2\text{CH}_2\text{S-CH}_2\text{CH(OH)CH}_2\text{N(CH}_3\text{)}_3\text{Cl}^-$ is used, desirable examples are

- 1) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 20% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 5 0.1 to 5, the pH has been adjusted to less than 4, and in particular to from 2 to 3, and the weight ratio of fluorocarbon silane to surfactant used to generate the hydrolysate is from 1:1 to 10:1; and 2) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 10% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 0.1 to 1, the pH has been 10 adjusted to from 4 to 7, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1.

In cases where an anionic surfactant represented by the formula

$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OSO}_3\text{NH}_4$ is used, desirable examples are 1) aqueous

- emulsions in which the fluorocarbon silane content is from 0.1 to 20% by weight, 15 the molar fraction of silicate with respect to the fluorocarbon silane is from 0.1 to 5, the pH has been adjusted to less than 4, and in particular to from 2 to 3, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1; 2) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 10% by weight, the molar fraction of silicate with 20 respect to the fluorocarbon silane is from 0.5 to 1, the pH has been adjusted to from 4 to 7, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1; and 3) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 20% by weight, the molar fraction of the silicate with respect to the fluorocarbon silane is from 0.1 to 5, the 25 pH has been adjusted to 7 or more, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1.

Adjustment of the pH is carried out using a suitable acid or alkali, such as hydrochloric acid or ammonia water.

The aqueous emulsions of the present invention can include additives such 30 as pigments, biocides, ultraviolet light absorbers, and antioxidants, within a range that does not affect the properties of the aqueous emulsion.

The aqueous emulsions of the present invention are applied and dried on a substrate such as a polymer substrate having pendant active hydrogen groups, such as polyesters and polyamides, wood, brick, concrete, stone, glass, ceramic tiles, aluminum sheet, stainless-steel sheet, natural and synthetic fibers, leather 5 and like.

Application of the aqueous emulsion onto the substrate is carried out by a known method such as dipping, spraying or spin coating. In cases where the aqueous emulsion is applied onto a glass substrate, a dipping method is preferable so as not to lose the clarity. Heating may also be carried out in order to accelerate 10 the drying step. Drying is generally carried out for 1 to 24 hours within a temperature range of from 100 to 300°C. Where necessary, the substrate onto which the aqueous emulsion has been applied and dried is washed with water after it has dried, thereby removing the remaining surfactant.

The aqueous emulsions of the present invention are useful in providing oil 15 and water repellent surfaces when coated and dried on a substrate. The coated surface is clear, smooth, and has excellent heat resistance. The coated substrates are useful in situations where the glass, fabrics, construction materials, and polymeric surfaces require oil and water repellency and clear coatings.

EXAMPLES

20 The aqueous emulsion of the hydrolysate of the fluorocarbon silane and the surfactant were prepared as in U.S. 5,550,184 wherein the fluorocarbon silane was emulsified in water with an effective amount of the indicated surfactant to retain the fluorocarbon silane in a substantially totally hydrolyzed state. Additional components were added to the emulsions as depicted in the examples 25 below.

WORKING EXAMPLES 1-7

The fluorocarbon silane hydrolysate used was a hydrolysate of a compound having the formula $R_f(CH_2)_2-Si\{-(O-CH_2CH_2)_2-OCH_3\}_3$ wherein R_f is a mixed perfluoroalkyl of formula $F(CF_2)_kCH_2CH_2-$ having the following

carbon atom distribution: 1-2% by weight k = 6, 62-64% by weight k = 8, 23-30% by weight k = 10, and 2-6% by weight k = 12 to 18. The surfactant used was a nonionic surfactant having the formula $R_F-CH_2CH_2-O-(CH_2CH_2O)_{11}-H$. The content within the aqueous emulsion was set at 30 parts by weight per 100 parts by weight of the fluorocarbon silane. The silicate used was 5 tetraethoxyorthosilicate (TEOS) or tetrakis [2-(2-methoxyethoxy)ethyl]silicate ($Si(DEGM)_4$). Adjustment of the pH was carried out by adding hydrochloric acid while using a pH meter. The stability of the aqueous emulsion thus prepared was measured by the method described below. The aqueous emulsion was prepared, 10 and one week later was examined to determine whether gelation or precipitation had occurred. Only in cases where it was free-flowing like water was it regarded as stable. Next, test pieces were fabricated using a glass substrate (commercial glass slides "Preclin Glass" trade name), manufactured by Matsunami Co. measuring 2.5 x 7.5 cm, and 1.2 mm thick. Because this glass is a washed glass, it 15 was used directly in testing. The application of the aqueous emulsion was carried out by means of dip coating. In dip coating the glass slide was lowered at a speed of 300 mm/min., held in the immersed state for 10 minutes, then drawn out at a speed of 10 mm/min. Drying after application was carried for 60 minutes at 200°C.

20 Using the test piece thus obtained, the clarity and water repellency of the coated surface were examined by the methods described below.

Clarity of Coated Surface

The surface of the substrate on which coating had been applied was visually examined with the unaided eye. When there was no change compared 25 with prior to coating, this was indicated as "clear." In cases where the substrate was glass, this was examined with an optical microscope (400X). When nothing could be seen, this was marked as "clear." When nothing could be seen with the unaided eye, but clouding was noted under microscopic observation, this was indicated as "slightly cloudy." In cases where clouding was apparent with the 30 unaided eye, this was indicated as "somewhat cloudy" or "cloudy," according to the degree of clouding. In the present invention, when the glass was observed to

be "clear" or "slightly cloudy," a clear surface layer was judged to have been obtained.

Water Repellency

5 A drop of pure water was added to the surface of the coated substrate, and the contact angle was measured with a contact angle analyzer (manufactured by Kyowa Kaimen Kagaku).

The stability of the aqueous emulsion, and the clarity and water repellency of the coated surface are each shown in Table 1 below.

Comparative Example A

10 In Comparative Example 1, an aqueous emulsion containing no silicate but containing the fluorocarbon silane of working Examples 1-7 was prepared. Using the aqueous emulsion thus obtained, test pieces were fabricated and tested in the same manner as in Working Examples 1-7. The stability of the aqueous emulsion, and the clarity and water repellency of the coated surface are given in Table 1.

15

Table 1

Example	Working Ex. 1	Working Ex. 2	Working Ex. 3	Working Ex. 4	Working Ex. 5	Working Ex. 6	Working Ex. 7	Comp. Ex. A
Type of silicate	TEOS	Si(DEGM) ₄	TEOS	TEOS	TEOS	TEOS	TEOS	—
pH of aqueous emulsion	2.0	2.0	2.0	2.9	3.0	2.0	2.0	2.0
Fluorosilane concentration (wt %)	10	10	10	10	10	15	2.5	10
Molar fraction	0.5	0.5	0.25	0.33	1.0	0.5	0.5	—
Stability	stable	stable	stable	stable	somewhat unstable	stable	stable	stable
Substrate	glass	glass	glass	glass	glass	glass	glass	glass
Clarity	clear	clear	slightly cloudy	clear	clear	clear	clear	somewhat cloudy
Water-repelling angle (degrees)	113	113	110	110	110	110	110	107
Water-repelling angle (°) after 100 hours at 300°C	113	113	—	—	—	—	—	99
Water-repelling angle (°) after 15 hours at 350°C	73	73	—	—	—	—	—	29

The molar fractions within this table indicate the molar fractions of tetraethoxyorthosilicate (TEOS) or tetrakis [2-(2-methoxyethoxy)ethyl]silicate (Si(DEGM)_4) with respect to the fluorocarbon silane. The same applies as well to Tables 2-7 that appear later in this specification.

5 Working Examples 1, 2, 4, 6 and 7 showed that the aqueous emulsions of the present invention have excellent stability, in addition to which the glass on which the aqueous emulsions of the present invention had been coated and dried were imparted with an excellent water repellency while maintaining the clarity of the glass. Moreover, Working Examples 1 and 2 showed that the water repellency 10 of the glass surface was maintained even after 100 hours in a 300°C oven, and that some degree of water repellency continued to remain even after 5 hours in a 350°C oven.

Upon comparing Working Examples 1-2 with Comparative Example A, it is apparent that when TEOS or Si(DEGM)_4 was added, the clarity became good 15 and the heat resistance was also improved.

When Working Example 1 and Working Examples 2 are compared, no difference between TEOS and Si(DEGM)_4 was observable in the stability of the aqueous emulsion or in the clarity or water repellency of the coated surface. However, the time required when preparing the aqueous emulsion (the time until 20 the emulsion becomes uniform) was respectively about three hours and about one minute. Hence, Si(DEGM)_4 was preferable in that it was able to greatly shorten the preparation time.

Working Example 3 showed that when the ratio of the silicate with respect to the fluorocarbon silane is low, the clarity tended to suffer. Working Example 5 25 showed that when the ratio of the silicate with respect to the fluorocarbon silane is high, the aqueous emulsion tended to become somewhat unstable.

Working Examples 1, 6 and 7 showed that, regardless of whether the fluorocarbon silane concentration was high or low, when the molar fraction of the silicate with respect to the fluorocarbon silane was 0.5, a stable aqueous emulsion 30 was obtained.

Working Examples 8-9

As in Working Example 2, the fluorocarbon silane hydrolysate used was a hydrolysate of a compound having the formula $R_f(CH_2)_2-Si\{-(O-CH_2CH_2)_2-OCH_3\}_3$, the silicate was tetrakis [2-(2-methoxyethoxy)ethyl]silicate 5 ($Si(DEGM)_4$), and the surfactant was a nonionic surfactant having the formula $R_f-CH_2CH_2-O-(CH_2CH_2O)_{11}-H$. As in Working Example 2, the content of surfactant within the aqueous emulsion was set at 30 parts by weight per 100 parts by weight of fluorocarbon silane. The pH was rendered alkaline by using ammonia water. The stability of the aqueous emulsion thus prepared was 10 examined in the same manner as in Working Example 2, and application of the aqueous emulsion as well as observation of the clarity and water repellency of the coated surface were carried out in the same manner as in Working Example 2. The results are presented in Table 2.

Comparative Examples B and C

15 In Comparative Examples B and C, aqueous emulsions containing no silicate but containing the fluorocarbon silane hydrolysate of working Examples 8-9 were prepared. Using the aqueous emulsion thus obtained, test pieces were fabricated in the same manner as in Working Examples 8 and 9. The stability of the aqueous emulsion, and the clarity and water repellency of the 20 coated surface are shown in Table 2.

Table 2

Example	Working Example 8	Working Example 9	Comparative Example B	Comparative Example C
Type of silicate	Si(DEGM) ₄	Si(DEGM) ₄	—	—
pH of aqueous emulsion	10.8	10.8	10.8	4.5
Fluorosilane concentration (wt %)	10	10	10	10
Molar fraction	0.5	1.0	—	—
Stability	stable	stable	stable	stable
Substrate	glass	glass	glass	glass
Clarity	clear	clear	somewhat cloudy	somewhat cloudy
Water-repelling angle (degrees)	112	115	110	108
Water-repelling angle (°) after 5 hours at 350°C	101	98	6	37

Upon comparing Working Examples 8 and 9 with Comparative Examples B and C, it is apparent that the clarity became good and the heat resistance was improved when Si(DEGM)₄ was added. Moreover, in Working Examples 8 and 9, even though the aqueous emulsion was alkaline rather than acidic, when a suitable amount of silicate was added, the clarity became good and the heat resistance was also enhanced.

Working Example 10, Comparative Example D

In Working Example 10 and Comparative Example D, aside from replacing the surfactant used in Working Example 2 and Comparative Example A with a nonionic surfactant having the formula C₉H₁₉-C₆H₄-O-(CH₂CH₂O)₅₀-H, the aqueous emulsions were prepared, the stability of the emulsions were observed, and the clarity and water repellency of the coated surfaces were examined, all in the same manner as in Working Example 2 and Comparative Example A, respectively. The results are given in Table 3.

Table 3

Example	Working Example 10	Comparative Example D
Type of silicate	Si(DEGM) ₄	—
pH of aqueous emulsion	2.0	2.0
Fluorosilane concentration (wt %)	10	10
Molar fraction	0.5	—
Stability	stable	stable
Substrate	glass	glass
Clarity	very slightly cloudy	somewhat cloudy
Water-repelling angle (degrees)	108	104
Water-repelling angle (°) after 5 hours at 350°C	57	37

From this it was apparent that even when another nonionic surfactant was used, the clarity due to silicate addition was enhanced and the heat resistance was also enhanced.

5 **Working Example 11, Comparative Example E**

In Working Example 11 and Comparative Example E, aside from replacing the surfactant used in Working Example 2 and Comparative Example A with a cationic surfactant having the formula R_f-CH₂CH₂SCH₂CH(OH)CH₂N(CH₃)₃Cl, the aqueous emulsions were prepared, the stability was observed, and the clarity and water repellency of the coated surfaces were examined, all in the same manner as in Working Example 2 and Comparative Example A, respectively. The results are given in Table 4.

Table 4

Example	Working Example 11	Comparative Example E
Type of silicate	Si(DEGM) ₄	—
pH of aqueous emulsion	2.0	2.0
Fluorosilane concentration (wt %)	10	10
Molar fraction	0.5	—
Stability	stable	stable
Substrate	glass	glass
Clarity	clear	somewhat cloudy
Water-repelling angle (degrees)	107	106
Water-repelling angle (°) after 10 hours at 350°C	46	20

From this it was apparent that the clarity due to silicate addition was enhanced and the heat resistance was also enhanced not only with the use of a nonionic surfactant, but even with the use of a cationic surfactant.

5 **Working Example 12, Comparative Example F**

In Working Example 12 and Comparative Example F, aside from replacing the surfactant used in Working Example 2 and Comparative Example A with an anionic surfactant having the formula C₁₂H₂₅(OCH₂CH₂)₄OSO₃NH₄ the aqueous emulsions were prepared, the stability was observed, and the clarity and water repellency of the coated surfaces were examined, all in the same manner as in Working Example 2 and Comparative Example A, respectively. The results are given in Table 5.

Table 5

Example	Working Example 12	Comparative Example F
Type of silicate	Si(DEGM) ₄	—
pH of aqueous emulsion	2.0	2.0
Fluorosilane concentration (wt %)	10	10
Molar fraction	0.5	—
Stability	stable	stable
Substrate	glass	glass
Clarity	clear	somewhat cloudy
Water-repelling angle (degrees)	107	107
Water-repelling angle (°) after 5 hours at 350°C	37	20

Working Example 12 showed that even when an anionic surfactant was used, the clarity and heat resistance were enhanced by the addition of silicate.

Working Examples 13-15, Comparative Example G

5 In Working Examples 13-15 and Comparative Example G, aside from using a stainless-steel sheet (2.5 x 5.0 cm, 1-mm thick) instead of the glass plate in Working Example 2 and Comparative Example A, the aqueous emulsions were prepared and observations were carried out in the same manner as in Working Example 2 and Comparative Example A, respectively. The results are given in
10 Table 6. The grades of the stainless steel used in the working examples and the comparative example are indicated in the table.

Table 6

Example	Working Example 13	Working Example 14	Working Example 15	Comparative Example G
Type of silicate	Si(DEGM) ₄	Si(DEGM) ₄	Si(DEGM) ₄	—
pH of aqueous emulsion	2.0	2.0	2.0	2.0
Fluorosilane concentration (wt %)	10	10	10	10
Molar fraction	0.5	0.5	0.5	—
Stability	stable	stable	stable	stable
Substrate	stainless steel 430	stainless steel 430A	stainless steel 304	stainless steel 430
Clarity	clear	clear	clear	clear
Water-repelling angle (degrees)	114	114	112	118
Water-repelling angle (°) after 100 hours at 350°C	120	121	118	98

It is apparent that, even when stainless steel was used as the substrate, the heat resistance was enhanced by addition of the silicate.

Working Example 16, Comparative Example H

5 In Working Example 16 and Comparative Example H, aside from using an aluminum sheet (JIS 1100, 2.5 x 5.0 cm, 1-mm thick) instead of the glass plate in Working Example 2 and Comparative Example A, the aqueous emulsions were prepared and observations were carried out in the same manner as in Working Example 2 and Comparative Example A, respectively. The results are given in
10 Table 7.

Table 7

Example	Working Example 16	Comparative Example H
Type of silicate	Si(DEGM) ₄	—
pH of aqueous emulsion	10.8	10.8
Fluorosilane concentration (wt %)	10	10
Molar fraction	0.5	—
Stability	stable	stable
Substrate	aluminum	aluminum
Clarity	clear	film adhesion was poor
Water-repelling angle (degrees)	113	101
Water-repelling angle (°) after 100 hours at 300°C	—	—
Water-repelling angle (°) after 5 hours at 350°C	123	13

Even when the substrate was aluminum, it was apparent that the addition of silicate enhances the clarity and also enhances the heat resistance.

Effects of the Invention

5 As explained above, coated surfaces obtained by coating and drying the fluorocarbon silane hydrolysate-containing aqueous emulsions of the present invention onto a substrate were clear and smooth, and were able to provide excellent water repellency and heat resistance. In addition, by adjusting both the molar ratio of fluorocarbon silane hydrolysate and silicate within the aqueous
10 emulsion and the pH according to the type of surfactant used, stable aqueous emulsions having good storability were obtained.

WHAT IS CLAIMED IS

1. An aqueous emulsion comprising
 - a) at least one hydrolysate of a fluorocarbon silane having the formula



5 wherein R_f is a perfluoroalkyl group having from 3 to 18 carbon atoms or a mixture thereof; each R' is independently an alkyl group having from 1 to 3 carbon atoms; p is from 2 to 4; and n is from 2 to 10; said hydrolysate generated in the presence of a surfactant, and

- b) a silicate having the formula



wherein each R is independently selected from the group consisting of OCH_3 , OCH_2CH_3 and $(OCH_2CH_2)_mOCH_3$ wherein m is 1 to 10.

2. The aqueous emulsion of Claim 1, wherein the content of said fluorocarbon silane in the aqueous emulsion is from 0.1 to 20% by weight.
- 15 3. The aqueous emulsion of Claim 2 wherein the molar fraction of said silicate with respect to said fluorocarbon silane is from 0.3 to 10.
4. The aqueous emulsion of Claim 3 wherein the weight ratio of said fluorocarbon silane and said surfactant used to generate the hydrolysate is from 1:1 to 10:1.
- 20 5. The aqueous emulsion of Claim 3 wherein the silicate is [2-(2-methoxyethoxy)ethyl] silicate.
6. The aqueous emulsion of Claim 5 wherein the surfactant used to generate the hydrolysate is a nonionic surfactant having the formula $R_fCH_2CH-O-(CH_2CH_2O)_{11}H$ wherein R_f is a perfluoroalkyl group having from 3 to 25 18 carbons, or a mixture thereof.
7. The aqueous emulsion of Claim 6 having a pH of less than 4.
8. A material that has been obtained by coating the aqueous emulsion of Claim 1 onto at least one surface of a substrate and drying.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/26019

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C17/30 C09D4/00 C09D183/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 513 727 A (TOYOTA) 19 November 1992 &JP04338137 (D) see claim 1 -----	1
A	US 5 552 476 A (HALLING) 3 September 1996 &US5550184 (D) see claim 1 -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 513727	A 19-11-1992	JP 2555797 B		20-11-1996
		JP 4338137 A		25-11-1992
		DE 69203783 D		07-09-1995
		DE 69203783 T		21-12-1995
		US 5424130 A		13-06-1995
US 5552476	A 03-09-1996	US 5550184 A		27-08-1996
		AU 693529 B		02-07-1998
		AU 1937695 A		18-09-1995
		DE 69506848 D		04-02-1999
		EP 0748323 A		18-12-1996
		JP 9509939 T		07-10-1997
		WO 9523804 A		08-09-1995